Why Don't Alcohol and Water Mix Very Well?

"The molecular structure of Alcohol-water mixtures"

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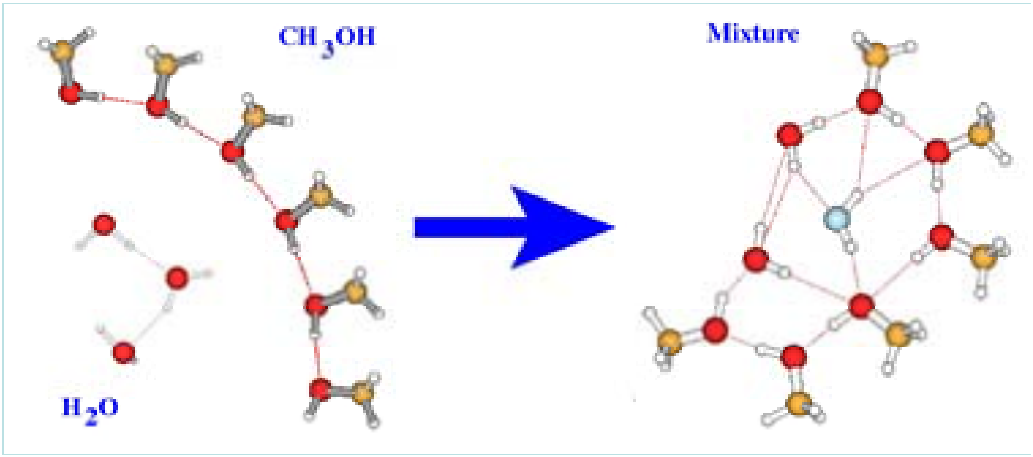


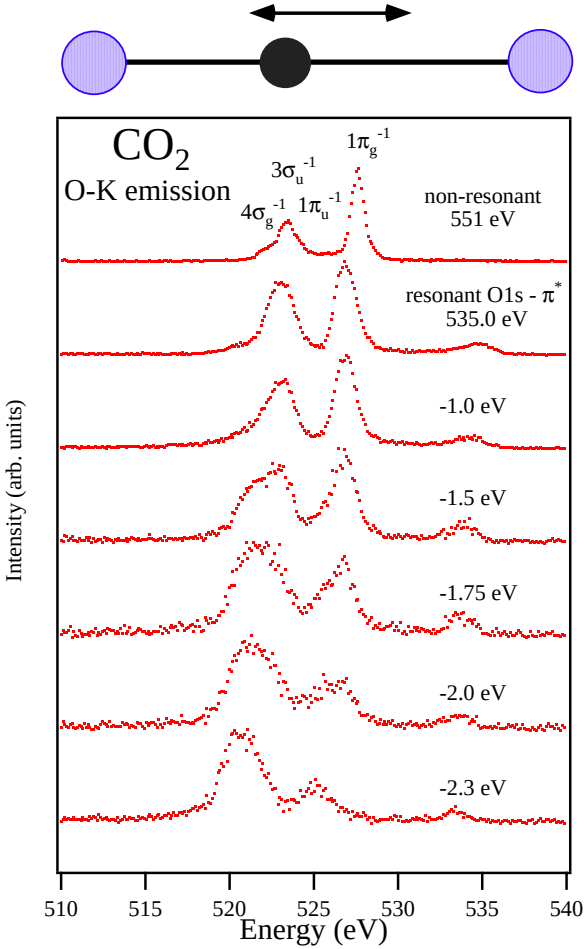
Collaborators

- **Y. Luo, S. Kashtanov, & Hans Ågren** (*Theoretical Chemistry, Royal Institute of Technology*)
- **A. Augustsson, J.-E. Rubensson, & J. Nordgren** (*Department of Physics, Uppsala University*)
- **D. K. Shuh** (*Chemical Sciences Division, Lawrence Berkeley National Laboratory*)

Molecules in gas and liquid phases

- Small molecules can be studied in great detail in the gaseous phase, where molecular interactions can be neglected, and consequently both their geometric structure and electronic structure are often well known.

- When the molecules interact in the liquid phase, our knowledge about these fundamental properties is very limited. The arrangement of the molecules change on a fast time scale: the geometry and the electronic structure of the molecules themselves vary, *i.e., the properties of the individual molecules are constantly changing*. Thus, from this perspective it is not surprising that there is still much to learn about common and simple liquids.



Skytt et al., Phys. Rev. Lett. 77, 5035 (1996).

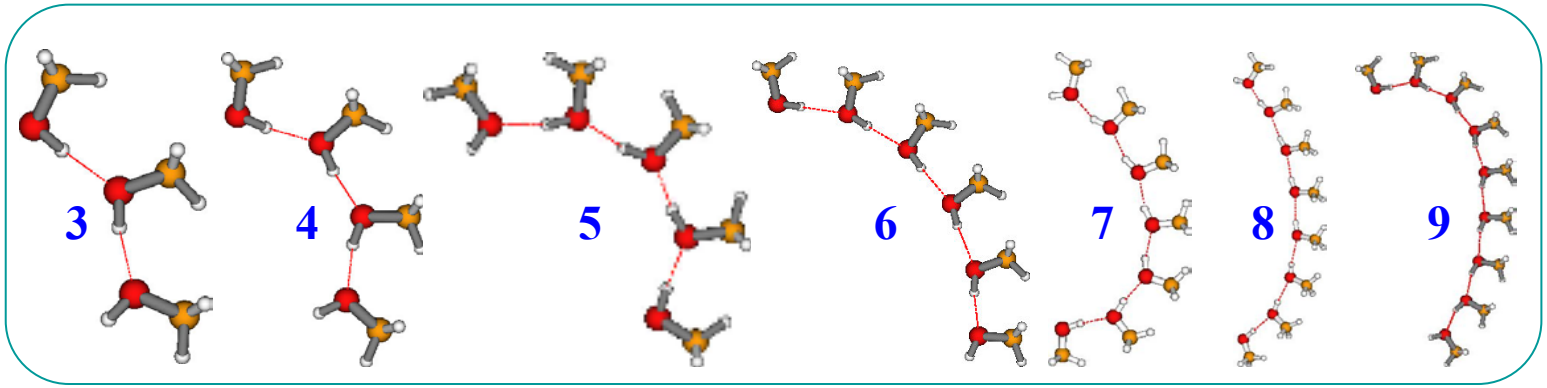
Microscopic Mixing of Liquids

- **Solvation in aqueous solution has been a most intensive studied problem in chemical physics. *The observed entropy increase upon mixing alcohol and water is much smaller than expected for an ideal solution.***
- **The anomalously small entropy increase upon solution of alcohols in water is traditionally explained in terms of a hydrophobic interaction with the apolar alcohol headgroups, which induces an ice-like structure in the surrounding water [***Frank et al., J. Chem. Phys.* ***13****, 507 (1945).*]
- **Early neutron diffraction data provides structure information of water cages around hydrophobic headgroups in solution [***Soper et al., Phys. Rev. Lett.* ***71****, 4346 (1993); Tsai et al., J. Chem. Phys.* ***104****, 9417 (1996); Dixit et al., J. Phys. Condens. Matter* ***12****, L323 (1999); Wakisaka et al., J. Mol. Liq.* ***90****, 175–184 (2001).*]
- **New neutron diffraction data demonstrated that incomplete mixing at the molecular level is essential to explain the negative excess entropy observed when methanol dissolves in water [***Dixit et al., Nature 416, 829 (2002).*]
- **We examine the influence of the intermolecular interaction on the local electronic structure of liquid methanol, water, and their solutions. Our study determines the molecular structure of both liquid methanol and water-methanol solutions in unprecedented detail, thus, forms the final leg of the "iceberg, cluster, molecular structure" story pertaining to alcohol-water solutions.**

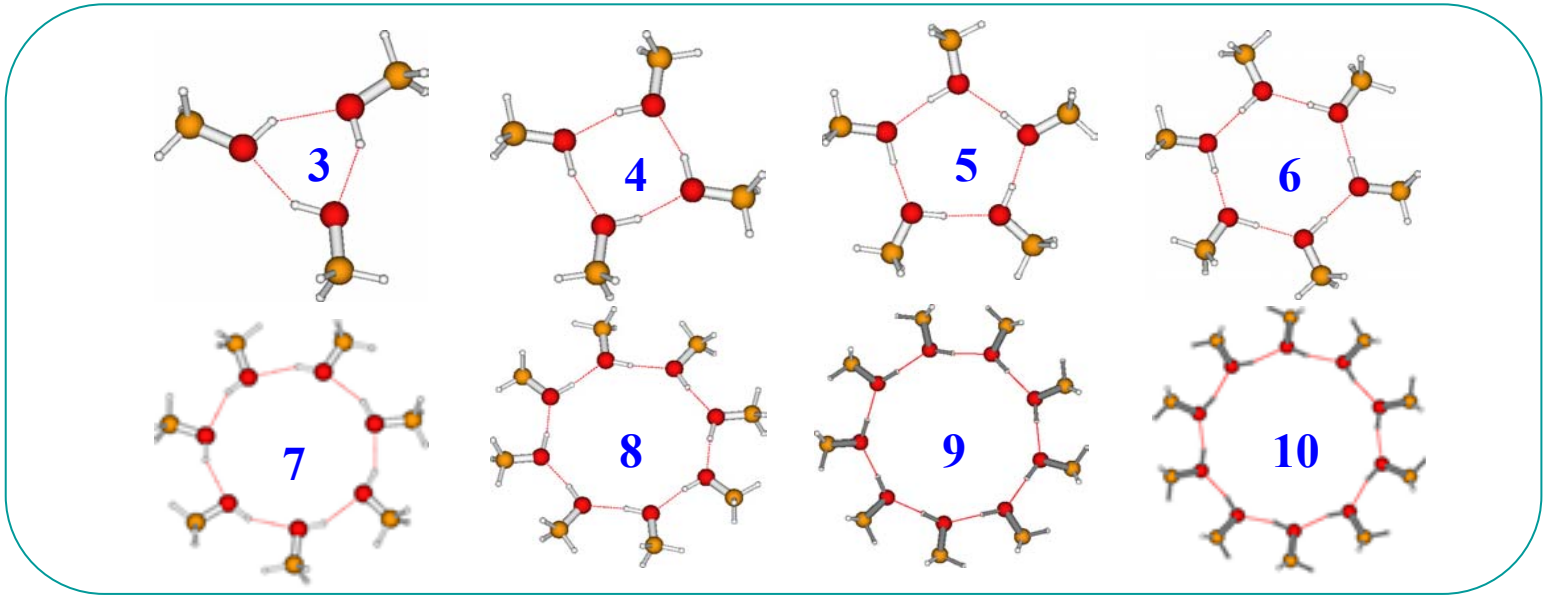
Molecular structure in liquid methanol

- Methanol crystal: infinite hydrogen-bonded chains; liquid methanol: non consensus after decades of studies
- The early hypothesis of cyclic structures by Pauling [*L. Pauling, The Nature of the Chemical Bond , Cornell Univ. Press, 1960*] has both been supported and contested by neutron diffraction analysis; the competing interpretation being that the majority of liquid molecules are ordered in chains with up to 10 members or linear trimer/tetramer chains
- Based on neutron diffraction data, it was found experimentally:
  - ✓ **chains up to ten molecules** with average of **six molecules** in liquid methanol [Yamaguchi, K. Hidaka, and A.K. Soper, *Molecular Physics* ***96****, 1159 (1999)*]*;* Haughney et al., *J. Phys. Chem.* ***91****, 4934 (1987)*; Svishchev et al., *J. Chem. Phys.* ***100****, 5165 (1994)* claimed the **same findings** based on MD calculation*;*
  - ✓ Sarkar, S. & Joarder, R. N., *J. Chem. Phys.* ***99****, 2032 (1993)* revealed a different picture of **cyclic hexamers** (six-rings);
  - ✓ Using the same diffraction data, Tanaka found **linear trimer and tetramer chains** [*Bull. Chem. Soc. Jpn.* ***58****, 270 (1985)*]

Molecular structures in liquid methanol

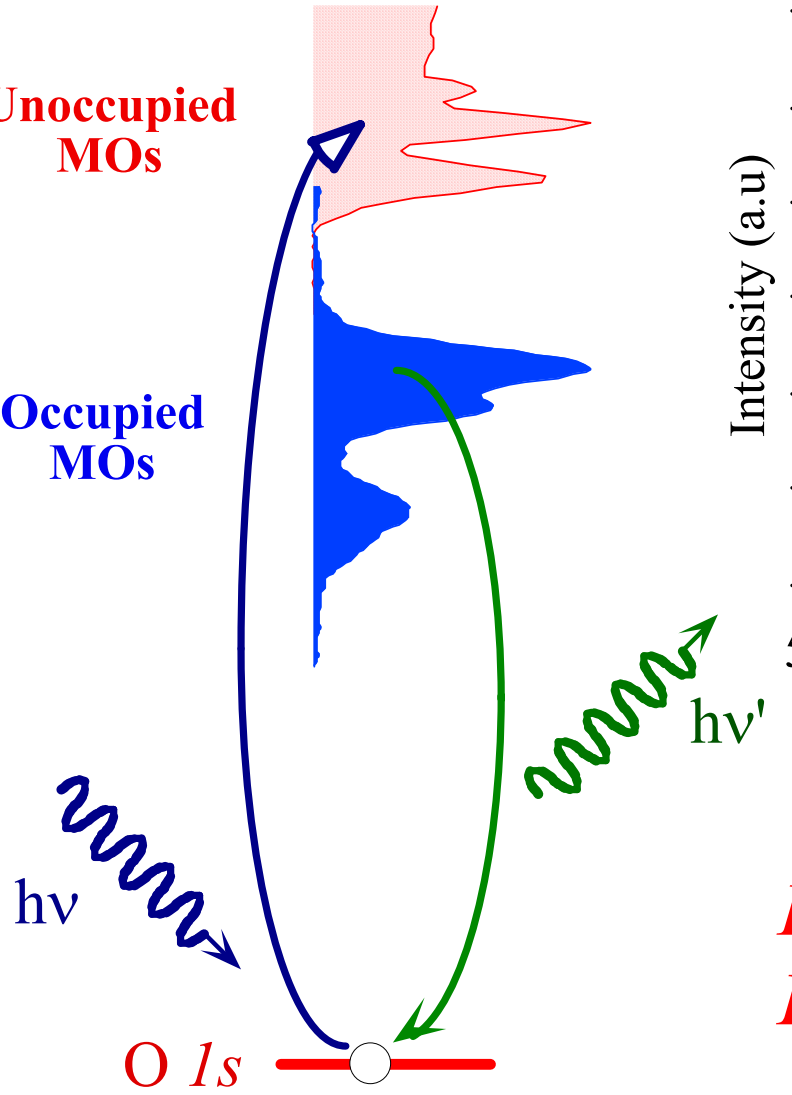


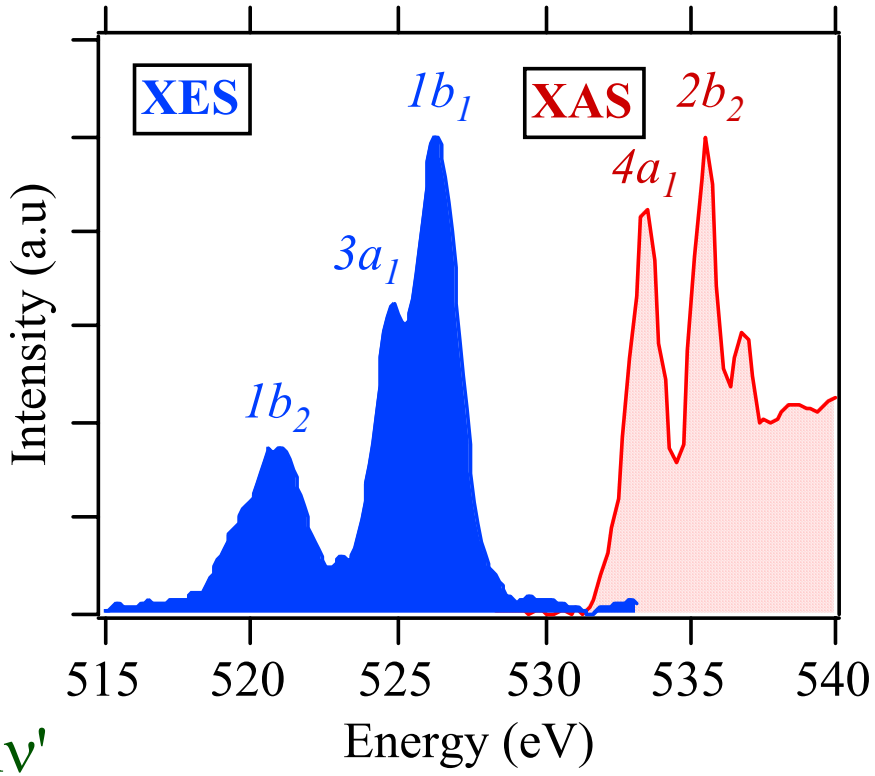
chains



rings

Soft-x-ray spectroscopy

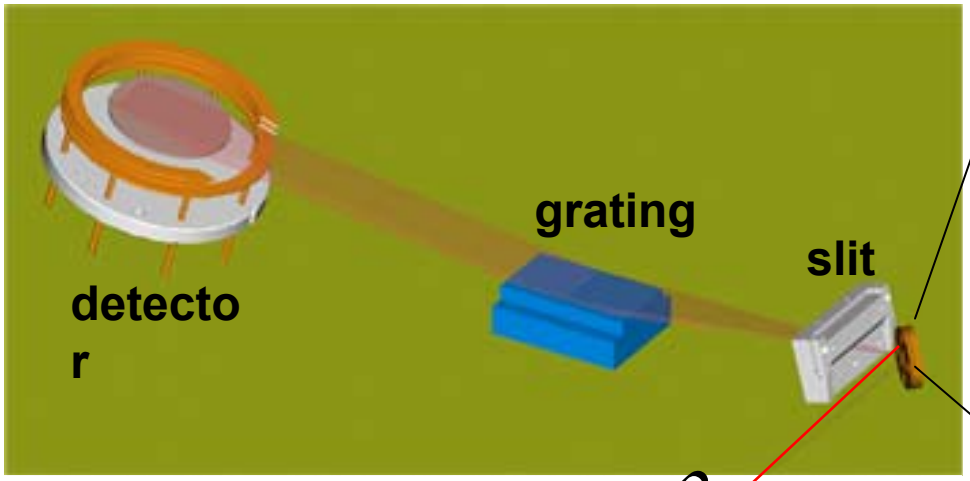


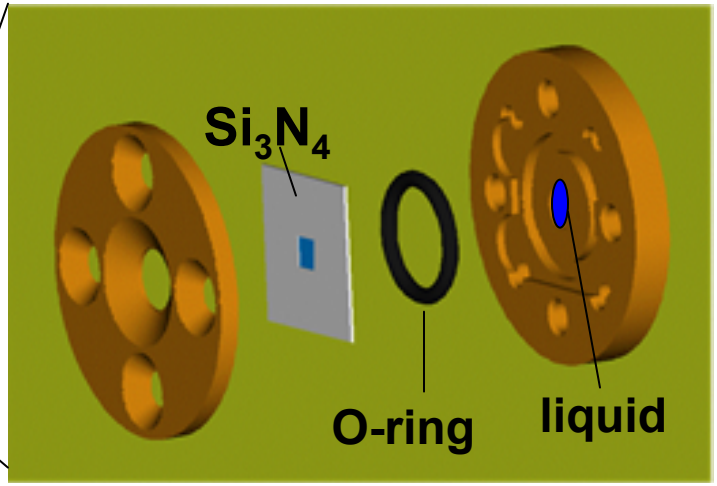


Primer excitation: 10^{-18} s

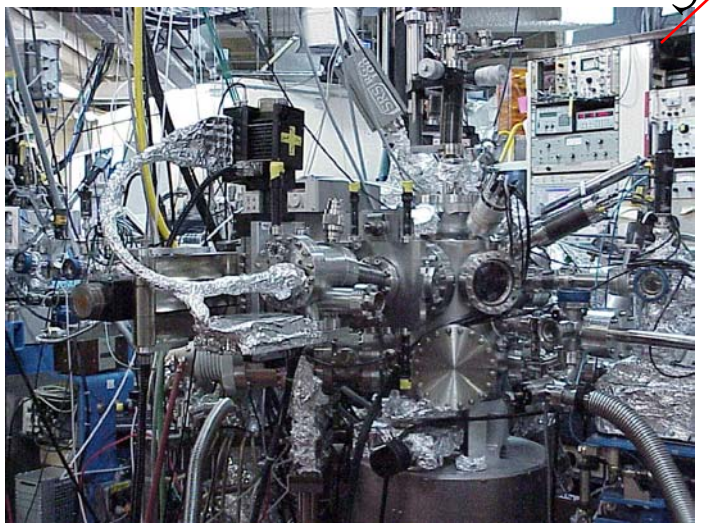
De-excitation: 10^{-15} s

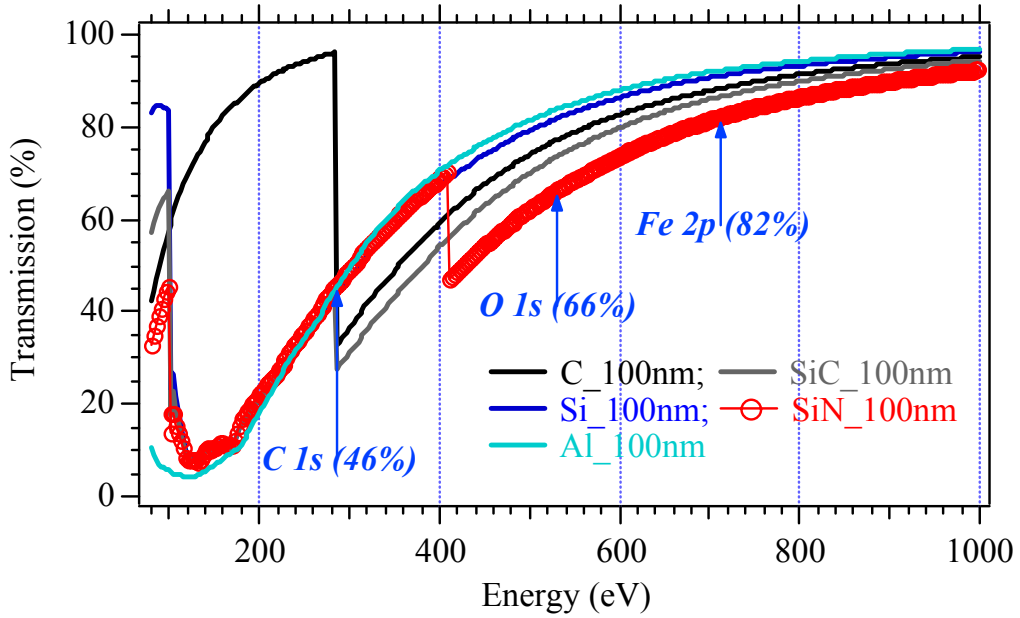
Wet samples in vacuum conditions





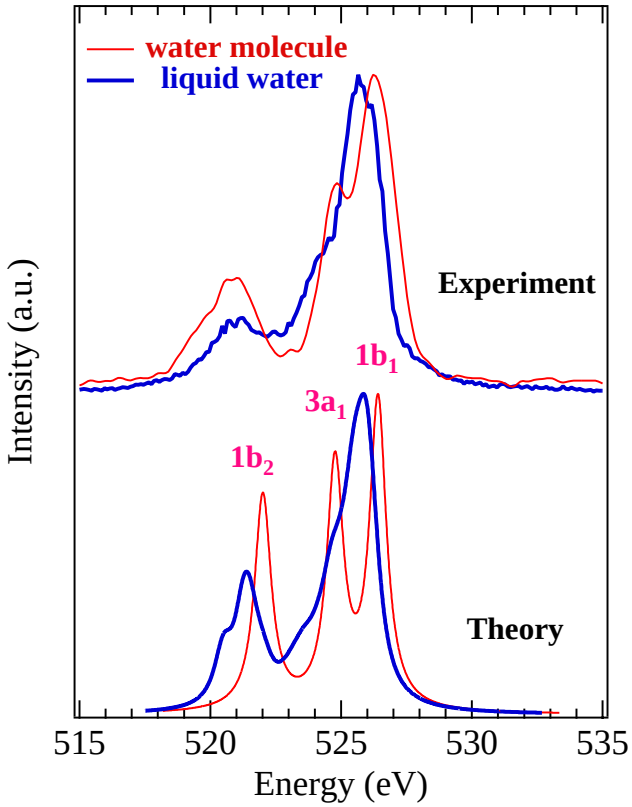
100nm Si_3N_4, ~4 µl liquid volume, 66% transmission @O1s, vacuum pressure < 1 x 10^{-9} Torr

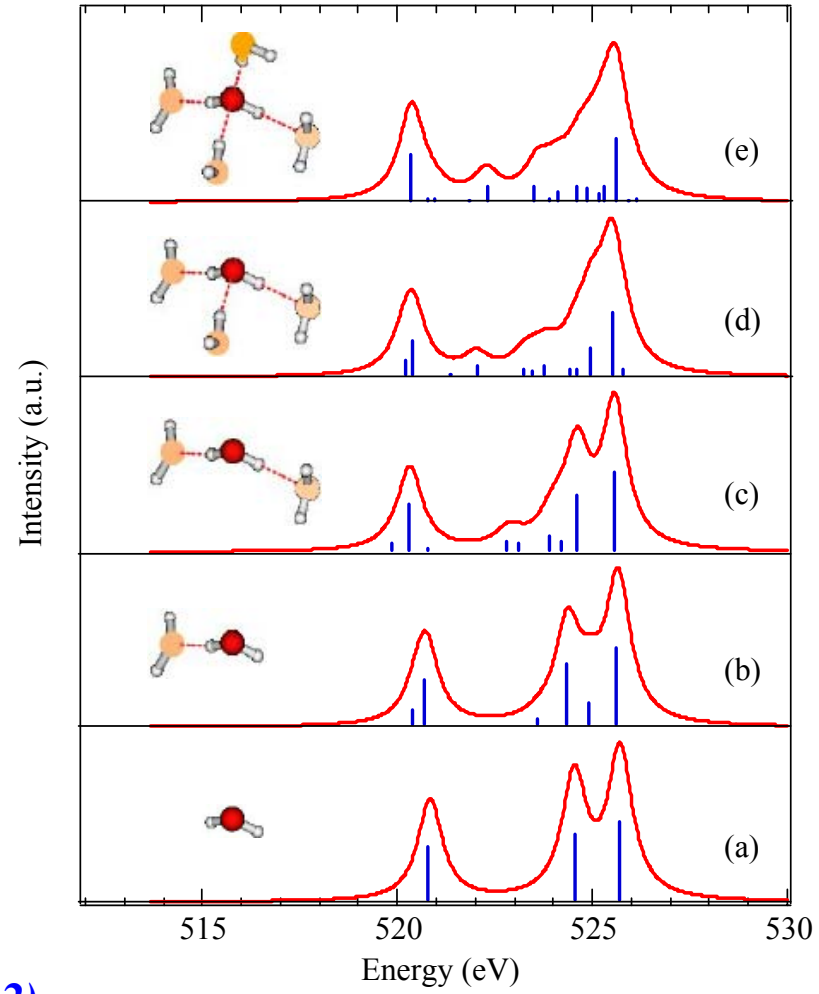




PHIOCA: photon-in and photon-out chemical analysis

H_2O molecule and liquid water



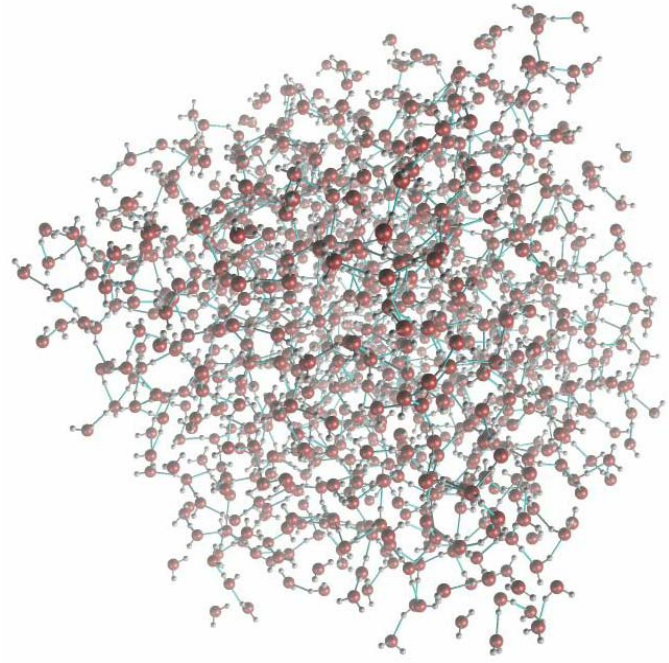


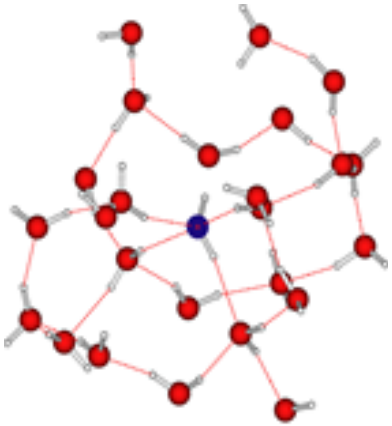
Hatree-Fock level with Sadlej basis set using the DALTON program on 32 nodes of the T3E computers at the NSC in Linköping

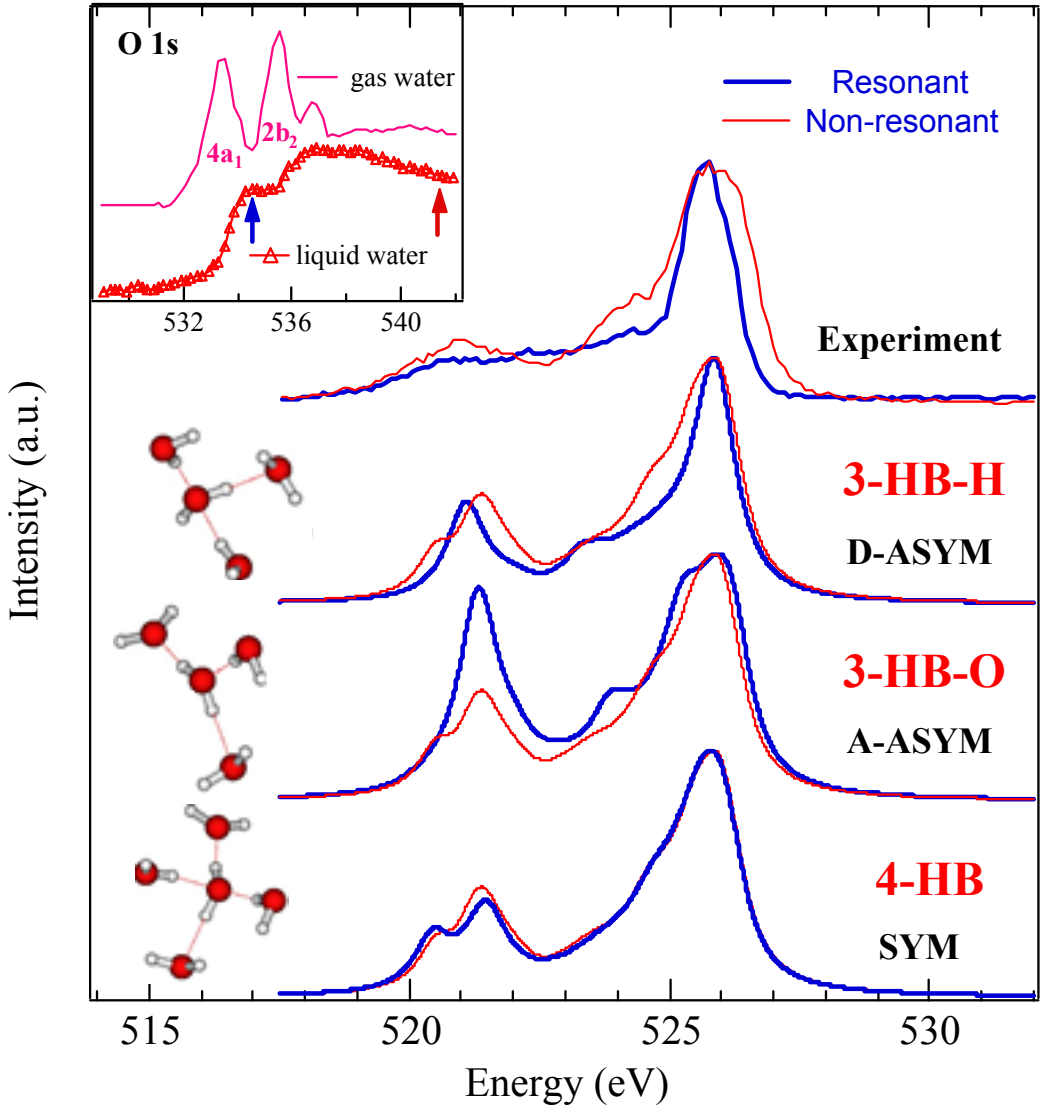
Guo et al., Phys. Rev. Lett.* 89, 137402 *(2002)

Finding: *an electron sharing takes place between water molecules. Such a sharing mainly involves the so-called $3a_1$ orbital, which is a mixing of oxygen 2p and hydrogen 2s atomic orbitals.*

Hydrogen bonding structure in liquid water

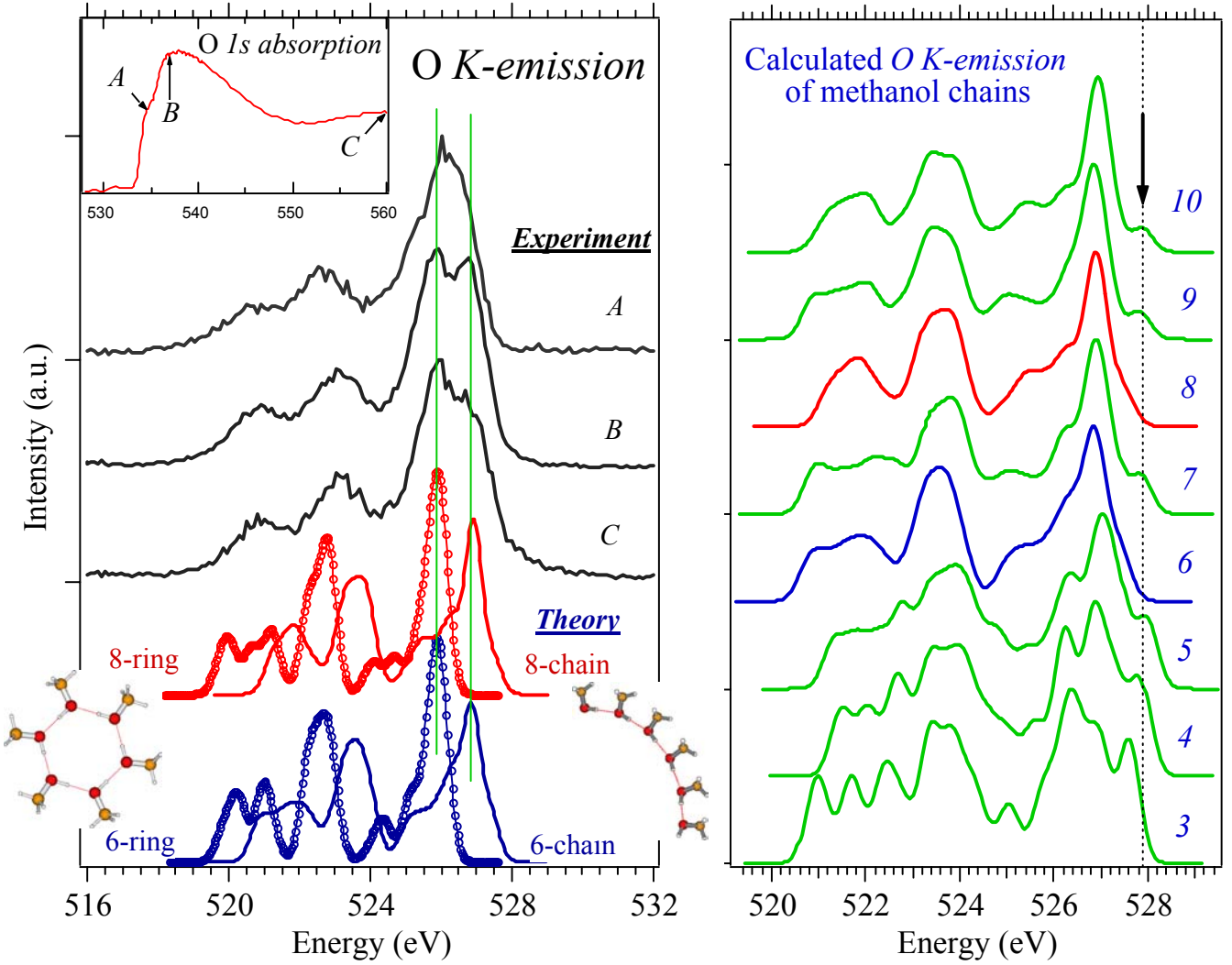






The X-ray emission spectra reveal the influence of hydrogen bonding on the local electronic structure of liquid water

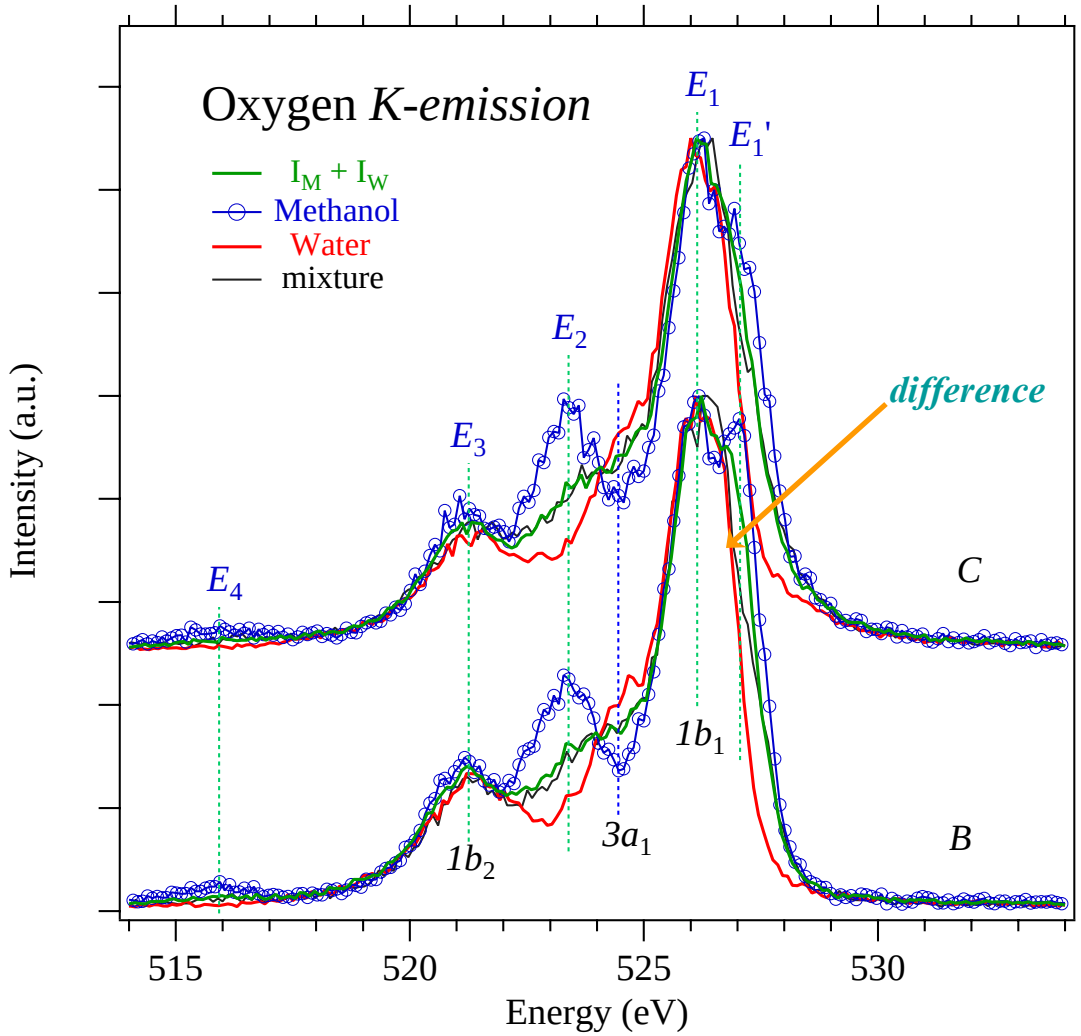
Molecular structure in liquid methanol



Guo et al., Phys. Rev. Lett. 91, 157401 (10 Oct. 2003)

Finding: *The structure of liquid methanol at room temperature is a combination of rings and chains each made up of either 6 or 8 methanol molecules*

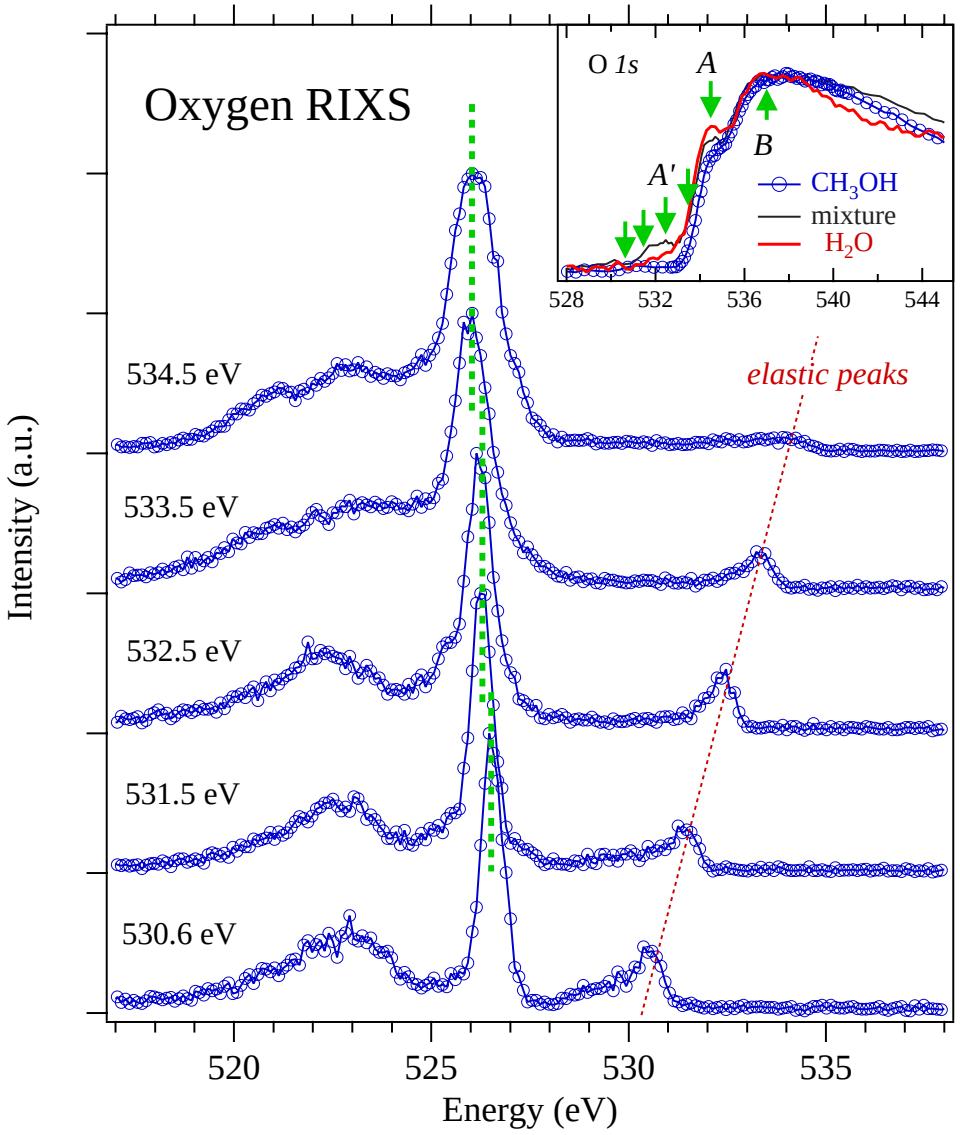
Incomplete mixing in alcohol-water solution



❑ *X-ray emission spectra of an equimolar mixture of methanol and water are compared to the spectra from the pure liquids. We find that a 1-to-1 combination of the pure liquid spectra reproduces the solution spectra to considerable detail. The spectra are very sensitive to the changes in the local electronic structure and this observation indicates incomplete mixing at the microscopic level.*

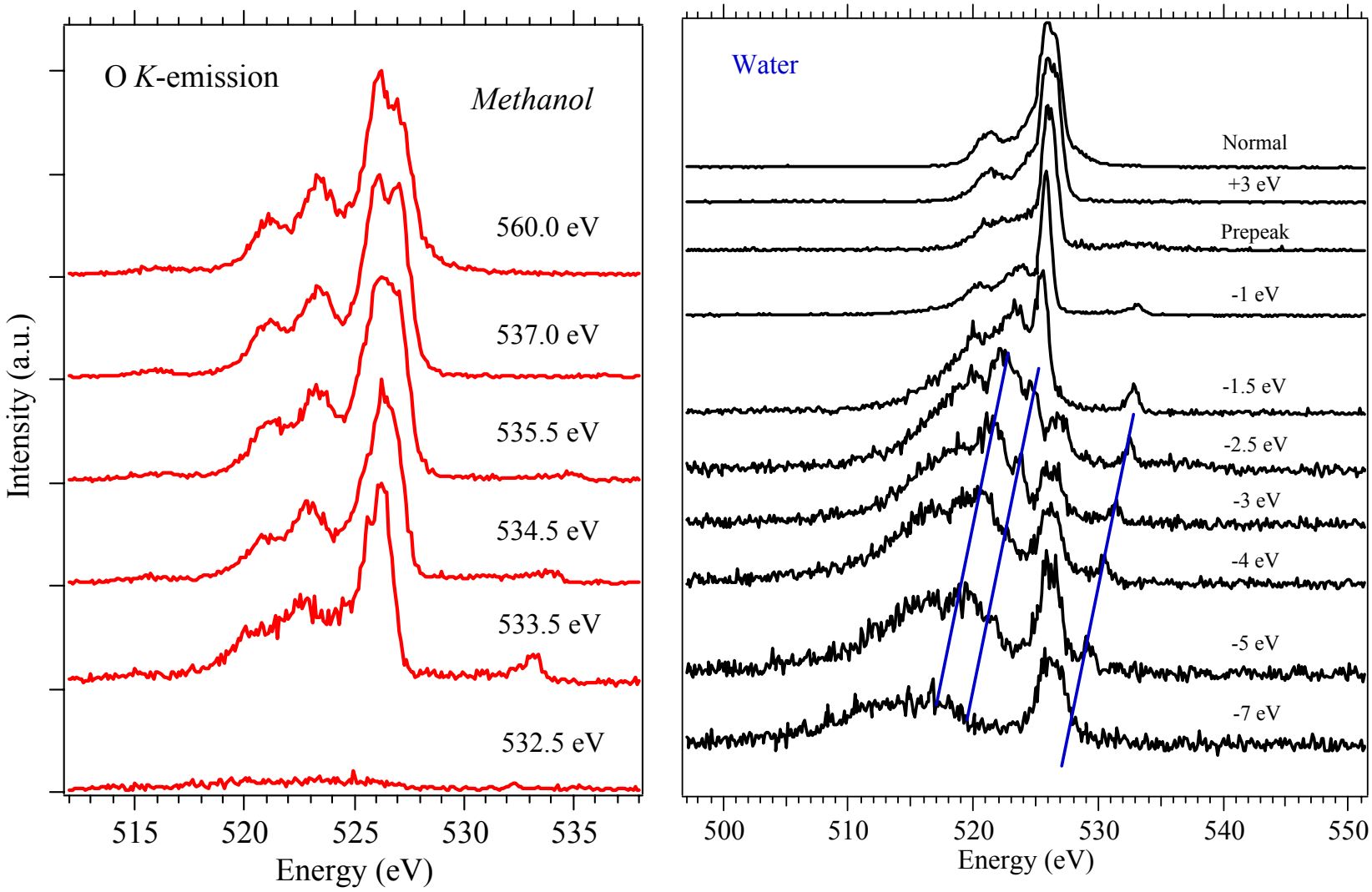
However, there is a significant discrepancy (indicated by arrow) when the excitation energy is selected to emphasize the chain structures (spectrum B). The solution spectrum shows a relative intensity decrease in the E_1' region, indicating a depletion of methanol chains in the solution.

RIXS of alcohol-water mixture



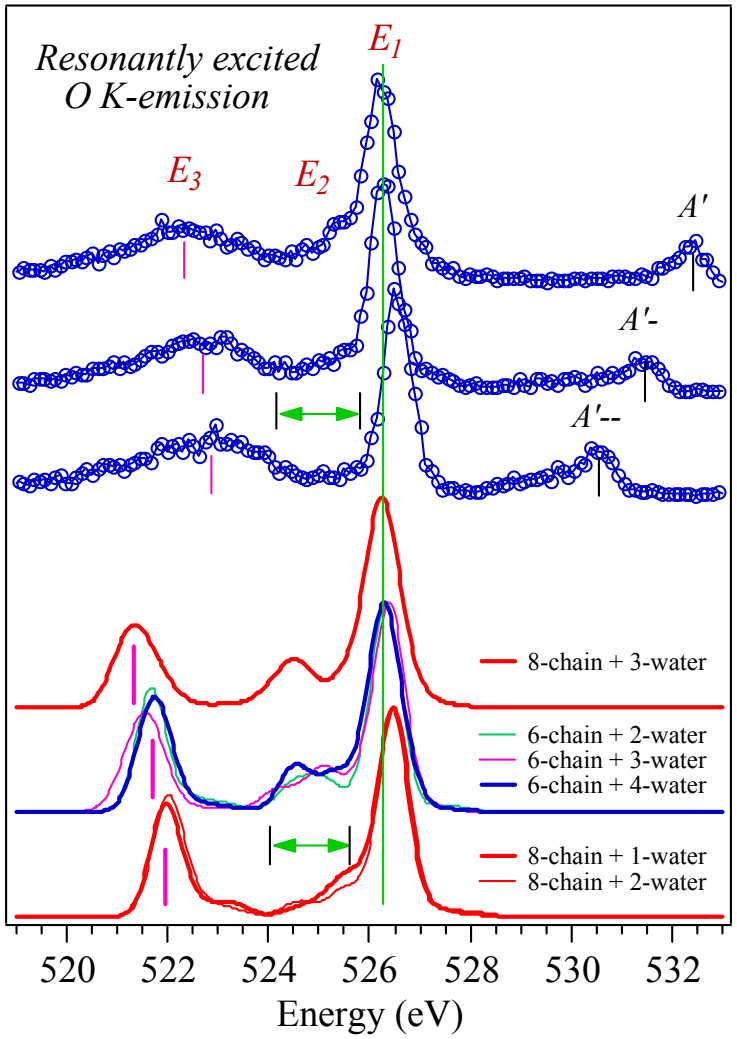
- The narrow spectral feature shown in the resonant emission spectra holds the key for identifying the structures. Based on the simulations of resonant emission spectra of water and methanol in both gas and pure liquid phases, this narrow spectral feature can only be generated from the emission of a water molecule that is "isolated" from the rest of the water network.
- We also know that there must be an interaction between water and methanol chains because there is a depletion of methanol chains in the solution. This results in a significant reduction of the number or possible trial structures. The new structures in alcohol-water mixture must be responsible for the spectral profiles.

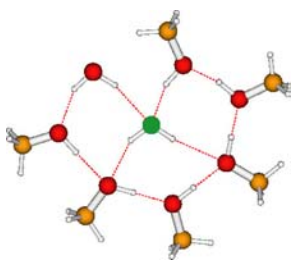
RIXS of liquid methanol and water

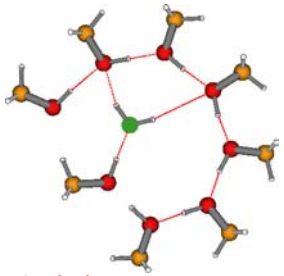


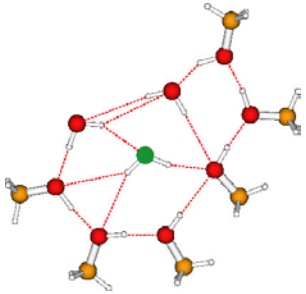
The RIXS spectra of liquid methanol and water under detuning conditions are different to their mixture

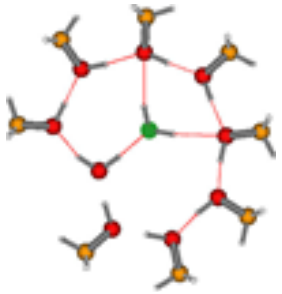
Molecular structure in alcohol-water mixture

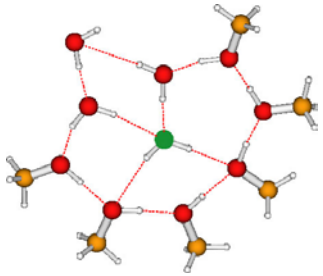


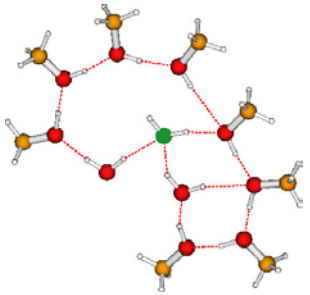

6-chain + 2-water


8-chain + 1-water


6-chain + 3-water


8-chain + 2-water


6-chain + 4-water


8-chain + 3-water

Theoretical spectra of a methanol molecule in various methanol-water local structures are computed. The structures presented above must be responsible for the spectral profiles.

Summary

- *In liquid water: A strong involvement of a_1-symmetry valence states in the hydrogen bonding indicates there is electron sharing between water molecules*
- *In liquid methanol: The molecules in the pure methanol liquid predominantly persist as hydrogen-bonded chains with 6 and/or 8 molecules, and as 6- and/or 8-molecule rings.*
- *For an equimolar water-methanol mixture, water and methanol molecules are incomplete mixing at the microscopic level.*
- *In addition, our results indicate a new mechanism for increasing order in the solution: water molecules bridge methanol chains to form rings with 6 and 8 methanol molecules.*

- *Many vital chemical and biological processes take place in aqueous solutions. We believe that the techniques have great general potential to provide new and valuable information in the quest for the microscopic origin of the properties of liquids and solutions; in particular the RIXS, will open new research opportunities in physical chemistry, nanotechnology, as well as in biochemistry and biology.*